

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets

(11)

EP 0 778 307 A2

EUROPEAN PATENT APPLICATION

(12)

(43) Date of publication:
11.06.1997 Bulletin 1997/24

(51) Int. Cl.⁶: C08J 3/22

(21) Application number: 96118821.6

(22) Date of filing: 25.11.1996

(84) Designated Contracting States:
DE FR GB IT

(30) Priority: 29.11.1995 US 564755

(71) Applicant: DOW CORNING CORPORATION
Midland Michigan 48686-0994 (US)

(72) Inventor: Fisher, Mark David
Midland, Michigan 48640 (US)

(74) Representative: Fleischer, Holm Herbert, Dr. et al
Patentanwälte Dr. H.-G. Sternagel,
Dr. H. Fleischer,
Dr. H. Dörries,
Sander Aue 30
51465 Bergisch Gladbach (DE)

(54) Method of making a polydiorganosiloxane-silica mixture, the resulting mixture and a room temperature curing sealant made therefrom

(57) A process of making a polydiorganosiloxane-silica mixture from a free-flowing, powdered, surface-modified, reinforcing silica-polydiorganosiloxane suitable, for example, for producing RTV silicone sealant compositions which are non-sag. These mixtures are made by combining, mixing and heating a reinforcing silica filler and a surface modifying agent at 90°C. to 180°C. using 0.1 to 0.5 parts by weight of the surface modifying agent per one part by weight of the silica. Polydiorganosiloxane is added gradually to the resulting fluidized filler over a time period of less than 10 minutes to yield the free flowing powdered reinforcing silica-polydiorganosiloxane. The final mixture is obtained by massing the concentrate and adding more polydiorganosiloxane to obtain a mixture which has from 8 to 20 weight percent silica filler. RTV silicone sealant compositions are obtained in 10 to 15 minutes from the initiation of our process.

EP 0 778 307 A2

Description

This invention provides a process of preparing a universal polydiorganosiloxane-silica mixture and a non-slump room temperature vulcanizable (RTV) silicone sealant therefrom.

5 RTV silicone sealants are used in the art for a variety of adhesive and weatherproofing applications. Many of these applications require a material consistency that allows it to be installed in the uncured state in a vertical configuration and to maintain that shape until cure has occurred. Such a sealant is said to have non-slump or non-sag properties. If a sealant sags or flows from its initial configuration, the desired weatherproofing or adhesive property is not obtained.

10 A typical silicone sealant formulation comprises a silicone polymer, a curing agent, such as a crosslinker or a combination of a crosslinker and a curing catalyst and a filler, such as a reinforcing silica filler or an extending filler. The reinforcing silica, such as fumed silica, is used to provide reinforcement to the polymeric network; to give a thixotropic property to the uncured composition; and to induce a higher tensile strength and tear strength in the cured product. It is generally known that the silica must be treated to yield a non-sag sealant composition. Without treatment, a slumpy or saggy sealant composition can result.

15 One way to prepare non-sag silicone sealants is to first react a crosslinker with a silicon-bonded hydroxyl endblocking group of a polydiorganosiloxane and to then follow with the addition of silica filler. Using this approach, crosslinker is used in an amount sufficient to react with the hydroxyl groups of the polydiorganosiloxane and the hydroxyl groups on the silica. This approach provides the desired non-sag sealant composition, but the process is limited to one type of cure chemistry, such as a sealant composition with organotriacetoxysilane crosslinker or organotrioximosilane crosslinker.

20 However, if a universal mixture could be prepared without the curing agent, i.e., crosslinker and curing catalyst, and if this mixture could be used as the basis for the preparation of a variety of sealant compositions having different curing agent chemistries, the advantages are many. For example, one universal starting mixture means that only minor changes on continuous mixing equipment are required and that change over from one sealant composition to another type can be readily accomplished. The number of required ingredients in inventory can thus be reduced and items of equipment formerly utilized can become available for other manufacturing processes. Also, the flexibility of the kinds of products made from only one starting material is advantageous for meeting new customer needs in a hurry.

25 To make a universal mixture viable for the manufacture of sealant compositions, it should be stable over the time period from immediately after its preparation to the time when the mixture is formulated into an RTV silicone sealant composition. "Stable", for the purposes of this invention, means that our mixture can be expediently used to formulate a sealant composition and the resulting composition will have a maximum slump of 0.51 cm (0.20 inch), as defined by ASTM D 2202, and preferably less.

30 It is desirable to prepare a non-sag, one-package, RTV, silicone sealant composition from a universal mixture which avoids during storage the well-known silica-polymer interaction problems, such as crepe hardening or structure formation. Generally, it is believed that the use of pretreated reinforcing silica fillers eliminates these silica-polymer interactions and provides a stable composition comprising polydiorganosiloxane and reinforcing silica filler. However, we have found that a stable universal mixture of silica filler and polydiorganosiloxane, wherein the siloxane polymer has a viscosity at 25°C. of 400 Pa · s or less, is not obtained with ordinary pretreated reinforcing silica fillers. In fact, commercially available pretreated silica fillers, such as Cabot TS-610(R) and Cabot TS-530(R), available from Cabot Corporation, 40 Tuscola, Illinois, require additional treatment to produce a mixture with long term stability, such that an acceptable sealant composition is produced for times as long as one year. TS-610 is a dimethyldichlorosilane treated fumed silica with a surface area of 120 (+/-20) m²/g and TS-530 is a hexamethyldisilazane treated fumed silica with a surface area of 200 (+/-40) m²/g.

45 One embodiment of this invention introduces a process for making a polydiorganosiloxane-silica universal mixture from a free-flowing, powdered, surface-modified, reinforcing silica-polydiorganosiloxane composition comprising:

- (i) combining, while mixing and heating, reinforcing silica filler having a surface area of 90 to 500 m²/g and having a median aggregate-agglomerate particle size less than 600 micrometers and a surface modifying agent of the formula $R'O(R_2SiO)_xR'$ wherein R is methyl, ethyl, vinyl, 3,3,3-trifluoropropyl or phenyl; each R' is selected from the group consisting of methyl radical, ethyl radical and acetyl radical; and x is a value of from 2 to 12 inclusive making a filler mixture where there is 0.1 to 0.5 part by weight of surface modifying agent per one part by weight of silica filler;
- 50 (ii) mixing the filler mixture at a temperature in the range of from 90°C. to 180°C. and maintaining the filler mixture in a fluidized powder state until the surface modifying agent is dispersed throughout the silica filler and the median aggregate-agglomerate particle size of the filler mixture is less than the median aggregate-agglomerate particle size of the silica filler, this mixing process not exceeding 30 minutes in duration and removing volatiles from the filler mixture during the mixing process;
- 55 (iii) adding gradually, with mixing, a polydiorganosiloxane having a viscosity measured at 25°C. of from 0.1 to 400 Pa · s to the modified silica filler obtained from step (ii) and completing the addition in less than 10 minutes after the

modified silica filler is obtained at the conclusion of step (ii), where the amount of polydiorganosiloxane is added to provide from 25 to 40 weight percent of silica filler, based on the total weight of the polydiorganosiloxane and the modified silica filler; thereafter

(iv) mixing until a uniform free flowing powder of a reinforcing silica-polydiorganosiloxane composition is obtained where the total mixing time of steps of (iii) and (iv) does not exceed 10 minutes; thereafter

(v) massing the uniform free-flowing silica-polydiorganosiloxane composition obtained from step (iv) until a paste consistency mixture is obtained, and

(vi) admixing gradually more polydiorganosiloxane making a uniform mixture having a higher concentration of polydiorganosiloxane than the free-flowing silica-polydiorganosiloxane (iv), with a silica filler content from 8 to 20 weight percent based on the total weight of the mixture.

Another embodiment of this invention provides a process for making a polydiorganosiloxane-silica mixture from a free-flowing, powdered, surface-modified, reinforcing silica-polydiorganosiloxane composition comprising:

(a) heating reinforcing silica filler having a surface area of 90 to 500 m²/g and having a median aggregate-agglomerate particle size less than 600 micrometers to a temperature in a range of 90°C. to 180°C., removing volatiles from the silica filler; thereafter

(b) adding to the heated reinforcing silica filler while mixing, a surface modifying agent of the formula R'O(R₂SiO)_xR' wherein R is methyl, ethyl, vinyl, 3,3,3-trifluoropropyl or phenyl; each R' is selected from the group consisting of methyl radical, ethyl radical and acetyl radical, and x is a value of from 2 to 12 inclusive, making a filler mixture where there is 0.1 to 0.5 part by weight of surface modifying agent per one part by weight of silica filler; and

(c) heating and mixing the filler mixture at a temperature in the range of 90°C. to 180°C. and maintaining the filler mixture in a fluidized state until the surface modifying agent is dispersed throughout the silica filler and the median aggregate-agglomerate particle size of the filler mixture is less than the median aggregate-agglomerate particle size of the silica filler, the mixing process not exceeding 30 minutes in duration, and removing volatiles from the filler mixture during the mixing process where a modified silica filler is obtained,

(d) adding gradually, with mixing, a polydiorganosiloxane having a viscosity measured at 25°C. of from 0.1 to 400 Pa · s to the modified silica filler of step (c) and completing the addition in less than 10 minutes after the modified silica filler is obtained at the conclusion of step (c), where the amount of polydiorganosiloxane is added to provide from 25 to 40 weight percent of silica filler, based on the total weight of the polydiorganosiloxane and the modified silica filler; thereafter

(e) mixing until a uniform, free-flowing, powdered, surface-modified, reinforcing silica-polydiorganosiloxane composition is obtained where the total mixing time of steps (d) and (e) does not exceed 10 minutes;

(f) massing the uniform free-flowing silica-polydiorganosiloxane composition (e) until a paste consistency mixture is obtained; and thereafter

(g) admixing gradually more polydiorganosiloxane making a uniform mixture having a higher concentration of polydiorganosiloxane than the uniform free-flowing silica-polydiorganosiloxane composition obtained in step (e) and the silica filler content of the mixture is from 8 to 20 weight percent based on the total weight of the mixture.

The process of this invention provides a universal mixture of polydiorganosiloxane and reinforcing silica which is used to make one-package, RTV, silicone sealant compositions which are non-sag. In the process of combining reinforcing silica filler with silanol terminated polydiorganosiloxane, non-sag silicone sealants are made from our universal mixture, if the reinforcing silica filler is expediently combined with a short chain polydiorganosiloxane surface modifying agent using certain process steps to modify the silica filler surface.

The short chain polydiorganosiloxane having silicon-bonded groups for the purposes of this invention is defined as a surface modifying agent of the formula R'O(R₂SiO)_xR' wherein R is methyl, ethyl, vinyl, 3,3,3-trifluoropropyl or phenyl; each R' is methyl radical, ethyl radical or acetyl radical; and x is a value of from 2 to 12 inclusive. The preferred surface modifying agents are those which are mixtures of molecules where at least 50 percent of the molecules have values for x of no more than 6. Surface modifying agents which have values of x of less than 6 provide foundation mixtures with longer stable storage times than those surface modifying agents having a value of x greater than 6. Particularly useful surface modifying agents are those which are mixtures of molecules where x has a value of about 4, and R is methyl, and R' is methyl or acetyl.

The reinforcing silica fillers are those which have a surface area of 90 to 500 m²/g and have a median aggregate-agglomerate particle size of less than 600 micrometers. The aggregate-agglomerate particle sizes are determined by a Coulter Particle Size Analyzer Model No. LS130, Hialeah, Florida. Many of these silica fillers are available commercially and are well known, such as fumed silica and precipitated silica. The silica fillers can be either untreated or treated. Treated silica fillers are also well known in the art and are available commercially, such as TS-610 and TS-530. The silica filler treatments include triorganosiloxy surface treatment from reaction with triorganochlorosilane, hexaorganosiloxane or hexaorganodisilazane; other silanes such as dimethyldichlorosilane; and various polydiorganosi-

loxanes that are endblocked with silicon-bonded hydroxyl groups or silicon-bonded alkoxy groups.

The surface modifying agent and the silica filler are combined while mixing and heating in step (i). They are combined such that there is from 0.1 to 0.5 part by weight of surface modifying agent per part by weight of silica filler. The amount of surface modifying agent used in making the modified silica filler which provides the most stable mixtures, i.e., those having the longest storage times and still producing a non-sag, one-package, RTV, silicone sealant composition, are those which have more than 0.25 part by weight of surface modifying agent per part of silica filler. The storage stability of the mixture and its ability to be formulated into non-sag sealant compositions is related to the chain length of the surface modifying agent. In both our universal mixture and the sealant composition, where everything is substantially equal except for the surface modifying agent, the higher the surface modifying agent chain length, such as x being 12, the more surface modifying agent is required to obtain equivalent storage stability for our mixture and the ultimate sealant composition slump, compared to that which is obtainable from using surface modifying agents with shorter chain lengths. Conversely, the shorter the surface modifying agent chain length, such as x being 2 to 4, the lower the concentration of surface modifying agent required to obtain equivalent storage stability for our mixture and the ultimate sealant composition slump.

The mixture of surface modifying agent and silica filler are fluidized (agitated) at a temperature of from 90°C. to 180°C., preferably from 150°C. to 180°C. The resulting filler mixture is maintained in a fluidized powder state until the surface modifying agent is dispersed throughout the silica filler and the median aggregate-agglomerate particle size of the filler mixture is less than the median aggregate-agglomerate particle size of the starting silica filler of step (ii). The filler mixture becomes more flowable and may be called "more fluffy" than the starting silica filler at this point of our process. At the more fluffy point, a modified silica filler is obtained. The density of the filler mixture may be reduced to 2 or 3 pounds per cubic foot (32-48 kg/m³) at this point of the process. This fluffy state is an indication that the surface modifying agent is dispersed throughout the silica filler. The mixing and heating step to obtain the modified silica filler should not exceed 30 minutes. Preferably, it is 5 minutes or less, and more preferably less than one minute. During this mixing and heating step the volatiles are removed. This is accomplished by means of a partial vacuum, by a nitrogen gas sweep or purge or using a combination of both partial vacuum and nitrogen gas sweep. When this mixing and heating step goes beyond 30 minutes of duration, no advantages are observed. The rate of dispersion of the surface modifying agent with the silica filler is increased by the addition of small amounts of hexamethyldisilazane, such as less than 0.1 weight percent based on the weight of the surface modifying agent.

The heating and mixing is accomplished in any mixing equipment which provides the necessary fluidization and agitation to maintain the surface modifying agent and the silica filler in a constant fluid state, heat as required, and removal of the volatiles. One such mixer is a Littleford™ Plowshear mixer/granulator, from Littleford Bros., Inc, Florence, Kentucky. This mixer provides a hurling and whirling action which are imparted by plow shaped mixing tools. The plow blades are coupled with high speed blending chopper blades which rotate at 3600 rpm and introduce high impact and shear. This particular mixer provides the required mixing for the preparation of our modified silica filler along with the ability to heat and remove volatiles. There is a window of mixing and heating time for which the resulting modified silica filler has excellent properties to provide storage stable products in which it is used. For instance, our universal mixture or the one-package RTV silicone sealant compositions which therefrom have non-sag properties. In this window of time, there is a relationship between the amount of surface modifying agent and the temperature present to provide excellent properties. At temperatures in the high part of the described range, smaller amounts of surface modifying agent are used to obtain the desired properties. Contrastingly, at temperatures in the lower part of the range, larger amounts of surface modifying agent are needed to achieve the same excellent results. "Storage stable" means that the products maintain their properties, within the rheology property profile as defined herein, throughout the time period beginning at the time when they are made, to the time when they are finally used to produce a RTV silicone sealant composition and through the time while the composition is cured. It is desirable to retain both the uncured properties, such as rheology and non-sag features of our RTV silicone sealant composition, as well as, the properties of the cured sealant, such as tensile strength, elongation, modulus and tear strength.

A preferred process for making the modified silica filler is to heat the reinforcing silica filler to a temperature in the range of 90°C. to 180°C. and remove volatiles from the silica filler, such as water which is often associated with silica fillers in step (a). The volatiles are removed by a partial vacuum, by a nitrogen gas sweep or by a combination of these two. The time is usually rather short for this step in view of the temperature used and with a gas sweep, the volatiles are readily removed in times of one minute or less. Preferably, the temperature is between 150°C. and 180°C. and the time is about one minute.

After the volatiles are removed, the heating and mixing is continued and the surface modifying agent is added in step (b), as defined above and in the amounts stated. The duration of the heating and additional mixing is as described above. The filler mixture is heated at a temperature in the range of 90°C. to 180°C., preferably 150°C. to 180°C., while maintaining it in a fluidized state until the surface modifying agent is dispersed throughout the silica filler and the particle sizes are observed to change as described above in step (c). This mixing process does not exceed more than 30 minutes in duration and the volatiles are removed as discussed previously to obtain a modified silica filler. Preferably, this mixing process is from 30 seconds to 60 seconds in duration. Steps (d), (e), (f) and (g) of the preferred process are the

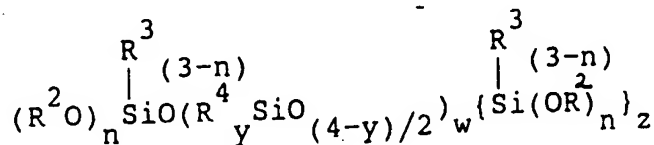
same as the steps (iii), (iv), (v) and (vi) as found in the above description.

After the modified silica filler is prepared, a polydiorganosiloxane having a viscosity measured at 25°C. of from 0.1 to 400 Pa · s is gradually added to the modified silica filler, such that, the addition is completed in less than 10 minutes, preferably less than 5 minutes (step iii). A sufficient amount of polydiorganosiloxane is added to provide a uniform free flowing powder having from 25 to 40 weight percent silica filler, based on the total weight of the powder. The modified silica filler and polydiorganosiloxane are then mixed until a uniform free flowing powder of polydiorganosiloxane and silica filler is obtained (step iv). The total mixing time in steps (iii) and (iv) should not exceed 10 minutes to obtain the uniform, free-flowing, powdered, polydiorganosiloxane-silica filler. By exceeding the 10 minute mixing time for steps (iii) and (iv), the powder will agglomerate creating lumps and other inconsistencies such that the powdered concentrate is not free flowing as needed and resulting in more difficult processing conditions when making sealant compositions.

In step (iii), the polydiorganosiloxane can be added incrementally to the modified silica filler obtained from step (ii). There does not seem to be any significant property variation to adding the polydiorganosiloxane continuously at a gradual pace or incrementally, except that by adding it continuously at a gradual pace an easier processing results to obtain a product.

The polydiorganosiloxane is selected from those having silicon-bonded hydroxyl groups at both ends or a mixture of polydiorganosiloxanes wherein more than 50 percent of the polymer molecules have silicon-bonded hydroxyl groups at both ends and the remaining polymer molecules contain silicon-bonded hydroxyl groups on one end and triorganosiloxy units on the other end. Those polydiorganosiloxanes which are mixtures of polydiorganosiloxanes with silicon-bonded hydroxyl groups on both ends and polydiorganosiloxanes with silicon-bonded hydroxyl groups on one end and triorganosiloxy units at the other are known in the art from U.S. Patent 3,274,145, which teaches polydiorganosiloxane mixtures having both silicon-bonded hydroxyl groups and triorganosiloxy groups. For this invention, when polymers having both silicon-bonded hydroxyl groups and triorganosiloxy groups are used in step (iii), those which are preferred have at least 80 percent of the ends terminated with silicon-bonded hydroxyl groups. The polydiorganosiloxanes preferably have a viscosity at 25°C. of from 5 to 100 Pa · s. The polydiorganosiloxanes comprise diorganosiloxane units of the formula R''_2SiO where R'' is a monovalent hydrocarbon radical or a halogenated monovalent hydrocarbon radical which are illustrated by alkyl radicals including methyl, ethyl, propyl, isopropyl, butyl, pentyl and hexyl; alkenyl radicals, such as vinyl, allyl and hexenyl; cycloalkyl, such as cyclopentyl or cyclohexyl; aryl such as phenyl or tolyl; and haloalkyl such as chloropropyl, trifluoropropyl and (2-perfluoropropyl)ethyl. The preferred polydiorganosiloxanes are those which have mostly methyl with minor amounts of vinyl and phenyl radicals. Although these polymers are defined as polydiorganosiloxanes, small amounts of other units such as monoorganosiloxanes or SiO_2 units may be present as frequently found in polydiorganosiloxanes as a result of the manufacturing methods used. By small amounts, it is meant that there are less than 5 mole percent of such units, preferably less than 2 mole percent.

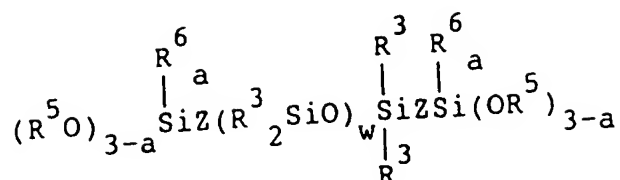
Other kinds of polydiorganosiloxanes can be used such as those which are endblocked with hydrolyzable containing silicon units, such as trimethoxysiloxy units, triethoxysiloxy units, methyldimethoxysiloxy units and methyldiethoxysiloxy units, as described in U.S. Reissue Patent 29,760, which more completely shows polyalkoxy terminated polydiorganosiloxanes and their method of preparation. These polyalkoxy terminated polydiorganosiloxanes are illustrated by the formula



in which R^2 is an aliphatic hydrocarbon radical or halogenated aliphatic hydrocarbon radical of from 1 to 8 inclusive carbon atoms, R^3 and R^4 are each selected from monovalent hydrocarbon radicals or monovalent halohydrocarbon radicals from 1 to 18 inclusive carbon atoms, n has an average value of from 2 to 3 inclusive, y has an average value of from 1.99 to 2 inclusive, z has an average value of from 1 to 1.01, the sum of y and z is 3, and w has a value such that the viscosity at 25°C. is from 0.1 to 400 Pa · s.

Some other polyalkoxy terminated polydiorganosiloxanes are those which contain divalent hydrocarbon linkages at the terminal portion of the polydiorganosiloxane, such as those described in U.S. Patents 3,175,993, 4,871,827 and 4,898,910, which show such polydiorganosiloxanes and methods of their preparation. These polydiorganosiloxanes have a formula.

5



10 in which each R^5 is methyl, ethyl, propyl or butyl, each R^6 is free of aliphatic unsaturation and is a monovalent hydrocarbon or monovalent halogenated hydrocarbon all of 1 to 18 inclusive carbon atoms, R^3 and w are as defined above, Z is a divalent hydrocarbon radical or combination of divalent hydrocarbon radicals and siloxane radicals and a is 0 or 1. Polydiorganosiloxanes which have other silicon-bonded hydrolyzable groups at their terminals may also be useful, for example acetoxo groups and ketoximo groups.

15 After the product of step (iv) is obtained, it is then massed until a paste consistency mixture is obtained (step v). This massing process is easily accomplished when the amount of silica filler in the concentrate is in the 25-40 weight percent range and especially when the viscosity of the polydiorganosiloxane is less than 50 Pa · s when measured at 25°C. The massing process requires equipment with high shear when the amount of silica filler is at the higher concentration, for example, 35-40 weight percent range and especially when the viscosity of the polydiorganosiloxane is greater than 50 Pa · s when measured at 25°C.

20 More polydiorganosiloxane is gradually admixed with the massed product of step (iv) to provide a universal mixture which contains from 8 to 20 weight percent of silica filler based on the total weight of the universal mixture, and preferably the mixture contains from 8 to 15 weight percent of silica filler. As the concentration of silica filler increases above 15 weight percent, the processing becomes more difficult as the viscosity increases and it requires greater energy to produce sealant compositions as well as initially making our claimed mixture. The concentration of the polydiorganosiloxane in this mixture is higher than in the free-flowing silica-polydiorganosiloxane composition. The polydiorganosiloxane is preferably added and mixed under conditions which keep the formation of voids at a minimum. This results in a quicker preparation of our universal mixture. When a paste consistency material is mixed with a fluid material, such as the polydiorganosiloxane, the incorporation of voids from a gas atmosphere is very likely to occur and extra care is required to keep the formation of such voids at a minimum. Other kinds of polydiorganosiloxanes can be used such as those which are endblocked with hydrolyzable containing silicon units, like the polyalkoxy terminated polydiorganosiloxanes described herein and further described by U.S. Reissue Patent 29,760; U.S. Patent 3,175,993 and U.S. Patent 4,871,827.

35 Our universal mixtures have a "plateau stress" value of greater than 700 dynes/cm², preferably more than 1,000 dynes/cm². This plateau stress value is a measure of polymer/filler interaction. After initial preparation plus any storage aging, our claimed universal mixtures are considered stable when the plateau stress value is greater than 700 dynes/cm². Sealant compositions made from such mixtures that have a plateau stress more than 1,000 dynes/cm², produce a composition with 0.5 cm (0.2 inch) flow or less when measured by ASTM D 2202. Our mixtures also have a shear-thinned viscosity of no more than 1,000 Pa · s at a shear stress of 50,000 dynes/cm², and preferably no more than 600 Pa · s where the viscosity is measured at 25°C. Therefore, the typical mixture will have a plateau stress of greater than 700 dynes/cm² and a shear-thinned viscosity of no more than 1,000 Pa · s. Preferred mixtures are those having a plateau stress of more than 1,000 dynes/cm² and a shear-thinned viscosity of no more than 600 Pa · s at 25°C.

45 Plateau stress values were determined on a Carri-Med™ Rheometer (Model CSL 500) using cone and plate. The flow method was used to determine these plateau stress values. The cone was a 0.5 degree, 2 cm diameter cone and the gap between the cone and the plate during testing was 13 micrometers (the test specimen thickness). Our claimed mixture was gently removed from the storage container. A few grams were placed on the temperature controlled bottom plate (at 25°C) before the plate was raised into position with the top cone to provide a specimen thickness of 13 micrometers. The test specimen was allowed to equilibrate for 1 to 5 minutes to reach the 25°C. condition. An initial stress of 100 dynes/cm² was applied to the test specimen. After equilibration, the shear stress was increased until 50,000 dynes/cm² was attained over a 5 minute period in a logarithmic stress sweep mode. This was called the up curve. Once 50,000 dynes/cm² was reached, this stress was held for 30 seconds. The shear stress was reduced to 100 dynes/cm² over a 5 minute period. This was called the down curve. The plateau stress value in dynes/cm² was the shear stress at the shear rate of 0.023 sec⁻¹ on the down curve. The shear-thinned viscosity was that viscosity measured when the shear stress was at 50,000 dynes/cm².

55 The product universal mixtures are non-sag and are used to make other silicone compositions which are non-sag, especially one-package, RTV, silicone sealant compositions. Such sealant compositions are prepared by adding a moisture hydrolyzable crosslinking silicone compound (as a curing agent) comprising a crosslinker or a crosslinker and a curing catalyst. The particular crosslinker can affect the non-sag property of the final RTV silicone sealant composition. Curing catalysts are used, as required, to provide the utility of cure for the one-package, RTV, silicone sealant com-

ade using our universal mixture.

sslinker is a silicon compound containing silicon-bonded hydrolyzable groups, preferably silanes. The silicon-bonded hydrolyzable group is exemplified by acyloxy groups such as acetoxy, octanoyloxy and benzoyloxy; ketoximo groups such as dimethyl ketoximo, methylethyl ketoximo, methyl amyl ketoximo, methyl isobutyl ketoximo and methyl n-butyl ketoximo; alkoxy groups such as methoxy, ethoxy and propoxy; alkenyloxy groups such as isopropenyloxy or 1-methylvinylloxy; amino groups such as dimethylamino, diethylamino, butylamino and cyclohexylamino; aminoxy groups such as dimethylaminoxy; and amido groups such as N-methylacetamido, N-ethylacetamido and N-methylbenzylacetamido. The crosslinkers can have three or more silicon-bonded hydrolyzable groups per molecule. When the crosslinker is a silane and when the silane has three silicon-bonded hydrolyzable groups per molecule, the fourth group is a silicon-bonded hydrolyzable silicon-bonded organic group. The silicon-bonded organic groups are exemplified by alkyl groups such as methyl, ethyl, propyl and butyl; cycloalkyl groups such as cyclopentyl and cyclohexyl; alkenyl groups such as vinyl; aryl groups such as phenyl and tolyl; aralkyl groups such as 2-phenylethyl; and groups obtained by substituting all or part of the hydrogen atom in the preceding organic groups with halogen. The preferred silicon-bonded hydrolyzable groups are preferably methyl.

The crosslinker can be a silane or siloxane and for siloxanes, the molecular structure can be straight chain, branched or cyclic. The silicon-bonded hydrolyzable groups are exemplified by acyloxy groups such as acetoxy, octanoyloxy and benzoyloxy; ketoximo groups such as dimethyl ketoximo, methylethyl ketoximo, methyl amyl ketoximo, methyl n-butyl ketoximo and diethyl ketoximo; alkoxy groups such as methoxy, ethoxy and propoxy; alkenyloxy groups such as isopropenyloxy and 1-ethyl-2-methylvinylloxy; amino groups such as dimethylamino, diethylamino, butylamino and cyclohexylamino; aminoxy groups such as dimethylaminoxy; and amido groups such as N-methylacetamido, N-ethylacetamido and N-methylbenzylacetamido.

Examples of silanes and siloxanes are exemplified by methyl trimethoxy silane, methyl triethoxy silane, vinyl trimethoxy silane, phenyl dimethoxy silane, 3,3,3-trifluoropropyl trimethoxy silane, methyl triacetoxysilane, ethyl triacetoxysilane, phenyl tripropionoxysilane, ethyl tris(N,N-diethylamino)silane, vinyl tris(N-methyl-N-diethylamino)silane, dimethyl bis(N,N-dibutyl-amino)silane, methyl tris(N-methylacetamido)silane, methyl vinylacetamido silane, vinyl tris(N-ethylacetamido)silane, methyl tris(N,N-diethylaminoxy)silane, phenyl tris(N,N-diethylaminoxy)silane, methyl tris(methylethylketoximo)silane, vinyl tris(methylethylketoximo)silane, 3,3,3-trifluoropropyl ketoximo)silane, methyl tris(isopropenoxy)silane, vinyl tris(isopropenoxy)silane, ethylpolysilicate, n-butylpolysilicate, dimethyl tetraacetoxysiloxane, pentamethyl tris(N,N-diethylaminoxy) cyclotetrasiloxane, hexamethyltris(dimethylaminoxy) cyclotetrasiloxane and mixtures thereof.

Other types of the crosslinkers can be triketoximosilanes and tetraketoximosilane, triacetoxysilanes and other triacylalkoxysilanes and tetraalkoxysilanes, silanes which contain mixtures of ketoximo and alkoxy groups. Various silanes having from 0 to 4 ketoximo groups per molecule and from 0 to 4 alkoxy groups per molecule. The total combined number of alkoxy and ketoximo groups per molecule are three or four. Silanes having both ketoximo groups and alkoxy groups in the same molecule are known from U.S. Patent 4,657,967 and 4,973,623. A tribenzamidossilane crosslinker is an example of another crosslinker which can be used in a one-package, RTV, silicone sealant compositions of this invention. These are illustrations of crosslinker silanes which can be used to make RTV silicone sealant compositions which are non-sag.

The choice of curing catalysts for a particular RTV silicone sealant composition depends upon the speed of cure required. For RTV silicone sealant compositions which contain oximosilanes or acetoxysilanes use a tin catalyst for curing such as diorganotin dicarboxylate compounds such as dibutyltin dilaurate, dibutyltin diacetate and dimethyltin diacetate. For the alkoxy silane crosslinker containing RTV silicone sealant compositions, the most preferred curing catalyst is a titanium catalyst such as tetrabutyltitanate, tetraisopropyltitanate, diisopropyl bis-(acetylacetonate) titanium, diisopropyl bis-(ethylacetoacetonate) titanate. Such crosslinkers and curing catalysts are well known to siliceticians and are well known in the silicone sealant art. A typical one-package, RTV, silicone sealant is made according to the present invention from the universal mixture, crosslinker, curing catalyst and may contain other ingredients which are known to be used in silicone sealants, such as extending fillers, pigments, fungicides, UV absorbers and other additives.

The RTV silicone sealant compositions of this invention are made from a universal mixture which is non-sag. Storage stability can be lengthened if the foundation mixture is kept cool, i.e. below 15°C. If, however, a conventional treated silica is used to make our universal mixture, a one-package, RTV, silicone sealant composition could be prepared which would not result in a non-sag product. Commercially available pretreated silicas, such as TS-610 and TS-530, can be used to make non-sag silicone sealant compositions, if a surface modifying agent is used and the processes of this invention are used. In addition to obtaining non-sag one-package RTV silicone sealant compositions from the universal mixture, the resulting sealant compositions have better clarity and better adhesion to plastic. One advantage of making non-sag silicone sealant composition from the mixture of this invention is the ability to change the cure chemistry, such as condensation reaction of silicon-bonded acetoxy functionality, to another cure chemistry such as condensation reaction of silicon-bonded ketoximo functionality. Heretofore, changing cure chemistry has required large amounts of waste and long non-productive time periods. However, with this invention, the

change over from one cure chemistry to another is fast and the amount of waste is small. The flexibility of being able to change quickly without loss of material or time is a great advantage. A significant feature of our process is the remarkably short time from the start of making the modified silica filler to the finished, one-package RTV silicone sealant composition, which can take less than 15 minutes of total time. This is a substantial reduction in time over conventional manufacturing processes for making silicone sealants wherein the silica modification is included in the process time calculations.

The following examples are presented for illustrative purposes and delineating the claims. In the following examples, "part" or "parts" are by weight, viscosities are as measured at 25°C. unless otherwise stated and Me is methyl radical.

Example 1

A universal mixture was prepared by mixing at room temperature 0.26 part of an alpha, omega-diacetoxy(octamethyltetrasiloxane) as the surface modifying agent per 1 part of a reinforcing silica filler having a BET surface area of 200 m²/g. After the surface modifying agent and silica filler were mixed, the mixture was heat to 95°C. for 30 minutes to obtain a surface modified silica filler. Enough of a polydimethylsiloxane having a viscosity of 16 Pa · s and having 85% of the endgroups being hydroxyl and 15% of the endgroups being trimethylsiloxy units (referred to hereinafter as Polymer A and prepared by U.S. Patent 3,274,145) was mixed with the resulting surface modified silica filler to provide a polydimethylsiloxane-silica powder having 32 weight percent of silica filler. A mixture was then prepared by massing the above powder and gradually adding more Polymer A to provide 12 weight percent of silica filler. A one package room temperature vulcanizing silicone sealant was prepared by mixing 95 parts of this mixture with 5 parts of a crosslinker mixture of 99.5 weight percent, which was 44 weight percent of methyltriacetoxysilane, 49 weight percent of ethyltriacetoxysilane, 7 weight percent of impurities and 0.5 weight percent of dibutyltin diacetate.

Slump values were determined using ASTM D 2202 as a test procedure. The extrusion rates were determined by using ASTM C 603 except that the test sealant was extruded through a nozzle with a 0.3175 cm orifice at a pressure of 620.5 kPa. The skin-over-time (SOT) in minutes was determined by spreading out a sample of the sealant composition, of 0.20 to 0.23 cm thick, the surface of the sample was touched lightly with a finger to determine if a skin had formed on the sample's surface. The SOT was the time period in minutes from the sample's initial layout until the finger could be touched lightly to the surface of the sample without sealant composition adhering to the finger. The tack-free-time (TFT) in minutes was determined by the ASTM C 679 test procedure. The plateau stress was determined as defined hereinbefore.

After eight days of storage in a container which sealed the sealant composition from atmospheric moisture, the following properties were determined:

Plateau stress = 1315 dynes/cm²
Extrusion rate = 296 g/min
Slump = <0.254 cm in 10 min
SOT = 7 min
TFT = 14 min

Example 2

The procedures of Example 1 were repeated to produce the same surface modified silica filler. Enough Polymer A was mixed with the resulting filler to provide a polydimethylsiloxane-silica powder having 32 weight percent of silica filler. A mixture was then prepared by massing the powder and gradually adding more Polymer A to provide 12 weight percent of silica filler. A one package room temperature vulcanizing silicone sealant was prepared by mixing 92.6 parts of this mixture with 3.12 parts of a ketoximosilane mixture of 70 weight percent of methyltri(methyl ethyl ketoximo)silane, 24 weight percent of methyl di(methyl ethyl ketoximo)silane, 0.5 weight percent of methyl dimethoxy(methyl ethyl ketoximo)silane, 5.5 weight percent of impurities, 1.51 parts of N-beta-aminoethyl-gamma-aminopropyltrimethoxysilane, 1.85 parts of methyl ethyl ketoxime, 0.79 part of tetraethyl orthosilicate and 0.15 part of dibutyltin dilaurate. The plateau stress, the slump, the extrusion rate, the SOT and the TFT were determined as explained in Example 1.

After eight days of storage in a container which sealed the sealant composition from atmospheric moisture, the following properties were determined:

Plateau stress = 4200 dynes/cm²
Extrusion rate = 290 g/min
Slump = <0.127 cm in 3 min and 0.127 cm in 10 min
SOT = 3 min
TFT = 9 min

Claims

1. A process for making a polydiorganosiloxane-silica universal mixture from a free-flowing, powdered, surface-modified, reinforcing silica-polydiorganosiloxane comprising:

(i) combining, while mixing and heating, reinforcing silica filler having a surface area of 90 to 500 m²/g and having a median aggregate-agglomerate particle size less than 600 micrometers and a surface modifying agent of the formula $R'O(R_2SiO)_xR'$ wherein R is methyl, ethyl, vinyl, 3,3,3-trifluoropropyl or phenyl; each R' is selected from the group consisting of methyl radical, ethyl radical and acetyl radical; and x is a value of from 2 to 12 inclusive, making a filler mixture where there is 0.1 to 0.5 part by weight of surface modifying agent per one part by weight of silica filler,

(ii) mixing the filler mixture at a temperature in the range of from 90°C. to 180°C. and maintaining the filler mixture in a fluidized powder state until the surface modifying agent is dispersed throughout the silica filler and the median aggregate-agglomerate particle size of the filler mixture is less than the median aggregate-agglomerate particle size of the silica filler, this mixing process not exceeding 30 minutes in duration, and removing volatiles from the filler mixture during the mixing process where a modified silica filler is obtained,

(iii) adding gradually, with mixing, a polydiorganosiloxane having a viscosity measured at 25°C. of from 0.1 to 400 Pa · s to the modified silica filler obtained from step (ii) and completing the addition in less than 10 minutes after the modified silica filler is obtained at the conclusion of step (ii), where the amount of polydiorganosiloxane is added to provide from 25 to 40 weight percent of silica filler, based on the total weight of the polydiorganosiloxane and the modified silica filler, thereafter

(iv) mixing until a uniform free flowing powder of a reinforcing silica-polydiorganosiloxane is obtained where the total mixing time of steps of (iii) and (iv) does not exceed 10 minutes, thereafter

(v) massing the uniform free-flowing silica-polydiorganosiloxane obtained from step (iv) until a paste consistency mixture is obtained, and

(vi) admixing gradually more polydiorganosiloxane making a uniform mixture having a higher concentration of polydiorganosiloxane, than the free-flowing silica-polydiorganosiloxane (iv), with a silica filler content from 8 to 20 weight percent, based on the total weight of the mixture.

2. The process according to claim 1 in which the polydiorganosiloxane in step (iii) is added incrementally to the modified silica filler of step (ii).

3. A universal mixture obtainable by the process of claims 1 or 2 which has a plateau stress of greater than 1000 dynes/cm² and a shear-thinned viscosity of no more than 600 Pa · s at a shear stress of 50,000 dynes/cm² and the plateau stress and shear-thinned viscosity are measured at 25°C.

4. A room temperature vulcanizable silicone sealant composition comprising the universal mixture according to claim 3 and further comprising a moisture hydrolyzable crosslinking silicone compound.

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 0 778 307 A3

(12)

EUROPEAN PATENT APPLICATION

(88) Date of publication A3:

18.03.1998 Bulletin 1998/12

(51) Int. Cl.⁶: **C08J 3/22**, **C08K 9/06**// **C08L83:04**

(43) Date of publication A2:

11.06.1997 Bulletin 1997/24

(21) Application number: **96118821.6**(22) Date of filing: **25.11.1996**

(84) Designated Contracting States:

DE FR GB IT(30) Priority: **29.11.1995 US 564755**

(71) Applicant:

DOW CORNING CORPORATION**Midland Michigan 48686-0994 (US)**(72) Inventor: **Fisher, Mark David****Midland, Michigan 48640 (US)**

(74) Representative:

Fleischer, Holm Herbert, Dr. et al**Patentanwälte Sternagel & Fleischer****Braunsberger Feld 29****51429 Bergisch Gladbach (DE)**

(54) **Method of making a polydiorganosiloxane-silica mixture, the resulting mixture and a room temperature curing sealant made therefrom**

(57) A process of making a polydiorganosiloxane-silica mixture from a free-flowing, powdered, surface-modified, reinforcing silica-polydiorganosiloxane suitable, for example, for producing RTV silicone sealant compositions which are non-sag. These mixtures are made by combining, mixing and heating a reinforcing silica filler and a surface modifying agent at 90°C. to 180°C. using 0.1 to 0.5 parts by weight of the surface modifying agent per one part by weight of the silica. Polydiorganosiloxane is added gradually to the resulting fluidized filler over a time period of less than 10 minutes to yield the free flowing powdered reinforcing silica-polydiorganosiloxane. The final mixture is obtained by massing the concentrate and adding more polydiorganosiloxane to obtain a mixture which has from 8 to 20 weight percent silica filler. RTV silicone sealant compositions are obtained in 10 to 15 minutes from the initiation of our process.

EP 0 778 307 A3



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 96 11 8821

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	EP 0 570 978 A (DOW CORNING TORAY SILICONE) * claims *	1	C08J3/22 C08K9/06 //C08L83:04
A	US 4 585 830 A (SWEET RANDALL P) * claim 1 *	1	
A	US 5 153 238 A (BILGRIEN CARL J ET AL) * claim 1 *	1	
A	US 4 724 167 A (EVANS EDWIN R ET AL) * claim 1 * * column 3, line 60 - column 4, line 19 *	1	
A	EP 0 676 445 A (SHINETSU CHEMICAL CO) * claim 1 *	1	
The present search report has been drawn up for all claims			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			C08J C08K C08L
Place of search		Date of completion of the search	Examiner
THE HAGUE		20 January 1998	Niaounakis, M
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X particularly relevant if taken alone Y particularly relevant if combined with another document of the same category A technological background O non-written disclosure P intermediate document</p> <p>T theory or principle underlying the invention E earlier patent document, but published on, or after the filing date D document cited in the application L document cited for other reasons S member of the same patent family, corresponding document</p>			